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Effect of Particle Sizes on the Impedance of Electrospun Tungsten Oxide Nanofibers

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Abstract

This work presents the fabrication and the impedance spectroscopy characterization of WO_3 nanofibers produced by an electrospinning technique. WO_3 nanofibers consisting of various particle sizes are obtained by adjusting synthesis parameters. We highlight the influence of nanoparticle sizes on electrical resistances of electrospun nanofibers. It is found that nanofibers with small particle size have significantly high electrical resistance at the grain boundary. This is due to a significant spanning of the electron-depletion layer as compared to the size of the conduction channel in the structure. The grain boundary resistances of nanofibers with larger particle sizes have shown to be independent of the sizes of nanoparticles. To obtain ultra-sensitive gas sensors, producing nanofibers with restrictedly small particle sizes is a key, since large changes in electrical resistances can take place upon reacting with target gas molecules.

Keywords: electrospinning; tungsten oxide; nanofibers; impedance spectroscopy

1. Introduction

Ultra-sensitive metal oxide-based gas sensors can be achieved by using the sensing elements that have high surface areas and large electron-depletion region. These would allow a significant change in their resistance upon interactions with targeted gas species. The fabrication of nanofiber structures of metal-oxide materials has been the subject of interest in recent years. An increase in surface-to-volume ratio as well as mesoporous nature of this structure offer unprecedented increase in the available sites for chemisorbed gas species and redox interactions at the surface [1].

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Among many metal-oxide materials, WO_3 is one of the most widely used due to its fast response and with high sensitivity towards different gases. It has also been reported that WO_3 is insensitive to water vapor at room temperature [2], allowing practical gas-detecting applications under humid environment to be performed. This work reports the fabrication of WO_3 nanofibers using an electrospinning technique. We emphasize the importance of the sizes of nanoparticles presented in the nanofibers to the impedance properties of the device.

2. Experimental

To fabricate WO_3 nanofibers, first a mixture of tungsten oxide precursor and a conducting polymer used to control viscosity of the solution are prepared. The precursor solutions are prepared by mixing ammonium metatungstate hydrate (AMH) in de-ionized water (DI) at 16.7% w/v, 33.3% w/v and 50.0% w/v concentrations. The conducting polymer is prepared by mixing polyvinyl alcohol (PVA) with de-ionized water (DI). Finally, the precursor and polymeric solutions are mixed and stirred vigorously for 24 h to obtain a homogeneous solution. The solution is then fed into the electrospining setup. The feed rate, the high voltage power supply, and the distance between the injection needle and the collector plate are fixed at 0.3 ml/min, 19.5 kV, and 15 cm, respectively. The nanofibers are electrospun onto pre-patterned Pt interdigitated electrodes. The resulting nanofibers are hot-pressed at 120ºC and calcined at 500ºC, 700ºC and 900ºC to remove the polymer and to carry out growth in some samples. Fig. 1a shows schematic diagram that summarizes the fabrication steps. Fig. 1b shows actual Pt interdigitated electrodes. Transmission electron microscope (FEI Tecnai G20) operating at 200 kV accelerating voltage is used to characterize the shape and size of WO_3 particles consisting in the nanofibers. Fig. 1c shows typical transmission electron microscope (TEM) image of WO_3 nanofiber produced in this experiment.

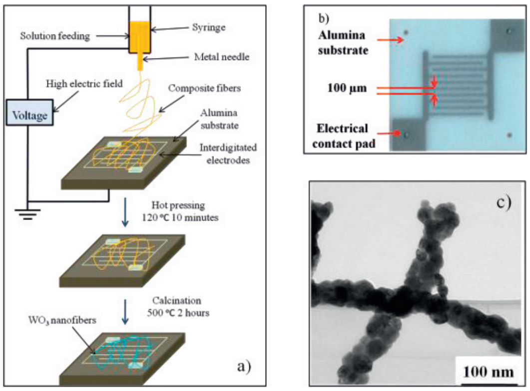

Fig. 1. (a) The fabrication steps of WO_3 nanofibers on the interdigitated electrodes using an electrospinning technique. (b) Platinum interdigitated electrodes with the gap of 100 µm on an alumina substrate and (c) typical TEM image of WO_3 nanofibers produced from AMH/PVA composite after calcination at 500ºC for 2 h.

The impedances of the WO_3 nanofibers are measured in air and under atmospheric pressure of O_2 at room temperature by employing an LCR meter (HP 4284A). The applied frequencies are varied between 20 Hz to 1 MHz, and the applied ac amplitude is 150 mV. The real part Re(Z) and the imaginary part Im(Z) of the complex impedance are recorded as the frequencies are swept. ZView™ software (v.3.3a, Scribner Associates Inc.) is used for extracting the impedances values: the bulk resistance R_b, the grain boundary resistance R_{gb}, and the grain boundary capacitance C_{gb}.

3. Results and discussions

Fig. 2a shows impedance spectroscopy characterizations of WO_3 nanofibers having particle sizes ranging from 40 nm to larger than 1000 nm. The impedance data are recorded in the real part Re(Z) and the imaginary part Im(Z) of the complex impedance as the frequencies are swept from 300 Hz to 1 MHz.

Fig. 2b shows the corresponding equivalent circuit of WO_3 nanofibers, which is obtained by extracting R-C parameters from the Nyquist plots. The electronic structure of WO_3 can be modeled correspondingly (Fig. 2c). The summary of synthesis conditions, R-C parameters, and particle sizes of the WO_3 nanofibers is shown in Table 1.

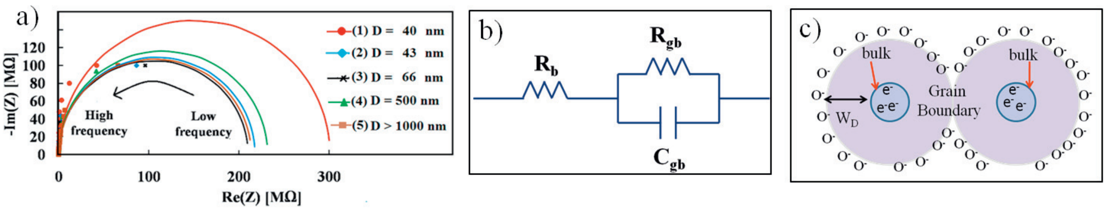

Fig. 2. (a) Impedance spectroscopy measurement and the fitted Nyquist plots of WO_3 nanofibers with various particle sizes. (b) The corresponding R-C equivalent circuit representation of WO_3 nanofibers: R_b, R_{gb}, and C_{gb} denote the bulk resistance, the grain boundary resistance, and the grain boundary capacitance, respectively. (c) Electronic structure representation of the WO_3 nanofibers.

Table 1. Summary of synthesis conditions, R-C parameters, and particle size of the WO_3 nanofibers.

Precursor Concentrations	Calcination Conditions	Particle Sizes (nm)	R-C parameters
16.7% AMH	500 °C 2 h	40 ± 7	R_b = 0.44 kΩ R_{gb} = 301.12 MΩ C_{gb} = 1.41 pF
33.3% AMH	500 °C 2 h	44 ± 14	R_b = 0.23 kΩ R_{gb} = 217.83 MΩ C_{gb} = 1.46 pF
50% AMH	500 °C 2 h	66 ± 13	R_b = 0.7 kΩ R_{gb} = 210.28 MΩ C_{gb} = 2.28 pF
50% AMH	700 °C 2 h	500 ± 100	R_b = 1.74 kΩ R_{gb} = 231.95 MΩ C_{gb} = 1.7 pF
50% AMH	900 °C 2 h	>1000 ± 300	R_b = 0.96 kΩ R_{gb} = 213.58 MΩ C_{gb} = 2.84 pF

From Table 1, the value of R_{gb} is several orders of magnitude higher than R_b. The results suggest that the electrical conduction of the WO3 nanofibers is largely dependent on the electron transport across the potential barrier at the grain boundary.

Fig. 3 shows the influence of the particles size (D) on the electrical resistance of resulting nanofibers. The resistance at the grain boundary has shown to be the limiting factor that controls the flow of electrons along the nanofibers. We can see that when D = 40 nm the nanofibers have large R_{gb} of 301.12 MΩ. Nanofibers with larger particle sizes have shown significantly lower electrical resistances, and appeared to be independent on the sizes of nanoparticles. This is due to the trivial impact of the size of the electron-depletion layer on larger nanoparticles.

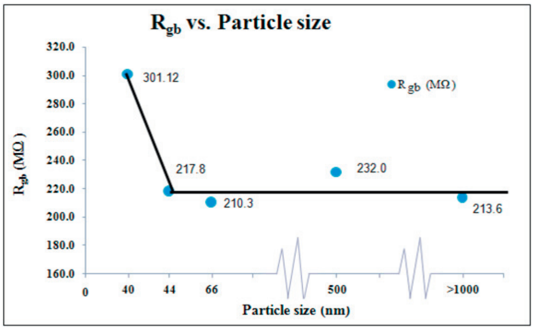

Fig. 3. Grain boundary resistance of WO_3 nanofibers measured at room temperature as a function of particle size of WO_3.

4. Conclusion

This work presents the fabrication steps and impedance spectroscopy characterization of WO_3 nanofibers. This information allows us to see that the conduction channel in this nanofiber is still large, as can be seen from a big difference between the bulk and the grain boundary resistances. Higher sensitivity gas sensor; thus, could be achieved from an even smaller grain, which would allow the space charge layer size to be larger as compared to the size of the particles in the nanofiber. Better understanding of electronic structure of materials will allow more optimized synthesis conditions for nanofibers, which will eventually lead to the production of high performance gas sensor.

Acknowledgements

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